SYNTHESIS AND PHOTOPHYSICAL STUDIES OF BIPOLAR HOST MATERIALS FOR PHOSPHORESCENT OLEDS

Submitted for partial fulfilment for

Master of Science in chemistry

By

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May 2014

Certificate

This is to certify that the project report entitled, "**Synthesis and Photophysical studies of Bipolar host materials for Phosphorescent OLEDs**", is being submitted to National Institute Technology, Rourkela by Mr SURAJ KUMAR PANIGRAHI having roll number 412cy2019 for partial fulfilment of the Master of Science degree, Chemistry, which is an original work carried out under my guidance and supervision. This work has not been submitted by him to any other University or Institute.

The present study is a valuable contribution for the advancement of knowledge in the field of Optoelectronics and lightening Industry.

In habit and character Mr SURAJ KUMAR PANIGRAHI is quite a fit and proper person for the further research work.

I wish him all success in his future life.

Date:

Prof. V.Sivakumar

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DECLARATION

I Suraj Kumar Panigrahi hereby declare that this project report entitled "Development of non-conjugated bipolar hybrid hosts for organic phosphorescent light-emitting diodes" is the original work carried out by me under the supervision of Dr. V.Sivakumar, Department Of Chemistry, National Institute of Technology, Rourkela (Odisha) and the present work or any other part thereof has not been presented to any other University and Institution for the award of any other degree regarding to my belief.

Suraj Kumar Panigrahi

412CY2019

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Suraj Kumar Panigrahi

Abstract

The remarkable progress of light-emitting organic semiconductors has led to the establishment of organic light-emitting diodes (OLEDs) as a major display technology. Furthermore, it has opened new directions for materials and devices, and exciting new applications. In the present work, three efficient organic green to yellow emitting bipolar materials, 3-(4-(diphenylamino)phenyl)-1-phenylprop-2-en-1-one (DPPO), 3-(4-(9H-carbazol-9-yl)phenyl)-1-phenylprop-2-en-1-one (CPPO) and 4-(bis(4-(diphenylamino)phenyl)amino))-1-phenylprop-2-en-1-one (BDPPO) were synthesized. The bipolar materials were characterized by ^{1}H NMR, ^{13}C NMR, Mass, UV-Visible, TGA-DTA and PL spectroscopy techniques. The synthesized phosphor materials are emitting green to yellow color with good emission intensity and can be used in the white light emitting LEDs.

ABBREVIATIONS

Alq_3……..	tris-(8-hydroxyquinoline)aluminium
CV …….	Cyclic voltammetry
DCM …….....	Dichloromethane
ECHB ……	Electron-conducting *I* hole-blocking
EL …….	Electro luminescence
E_T	Triplet energy
EQE ……..	External quantum efficiency
HOMO …….....	Highest occupied molecular orbital
LUMO ……..	Lowest unoccupied molecular orbital
ITO ……	Indium tin oxide
MEH-PPV ……	poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene]
Mp …….	Melting point
NEt_3	Triethylamine
NMR …….	Nuclear magnetic resonance
OLEDs ……..	Organic light-emitting devices
PBD ……..	5-(4-biphenyl)-2-(4-tert-butylphenyl)-1 ,3,4-oxadiazole
PEDOT …….	poly(ethylenedioxy-thiophene)
PET ……...	poly(ethyleneterphthalate)
PL ……..	Photoluminescence
PPV ……...	poly(p-phenylenevinylene)
Ppy ……	poly(pyridine-2,5-diyl)
PPym …….	poly(pyrimidine-2,5-diyl)
PVK ……..	poly(vinylcarbazole) 32
TIPD …….	2,2 ',2"-(1 ,3,5-benzenetriyl)tris{l-phenyl)-1 H-benzimidazole
Tg ……..	Glass transition temperature
THF ……...	Tetrahydro furan
TLC ……...	Thin layer chromatography
Uv …….	Ultraviolet
Vis …….	Visible

Chapter 1

Background and Introduction

1.1. Luminescence:

Luminescence is the production of light from a compound (either organic or inorganic). Luminescence can occur following a number of different mechanisms. Organic compounds suitable for OLED applications will display photoluminescence and electroluminescence.

In order for a material to emit energy in the form of light energy it needs to be in a higher energy (excited) state which can come back to the ground state by releasing energy in the form of a photon or through a nonradiative pathway. These excited states can be formed by photoexcitation (photoluminescence) or electronic excitation (electroluminescence).

1.1.1. Photoluminescence:

In photoluminescence an incident photon excites an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). A molecular excited state is formed from which the electron can then decay back to the HOMO. This process can be radiative or non-radiative, i.e., a photon can be released or a non-radiative process can aid the relaxation of the electron to the HOMO. The energy of the photon will be equal to the energy difference between the HOMO and LUMO. A schematic of photoluminescence can be seen in below fig.

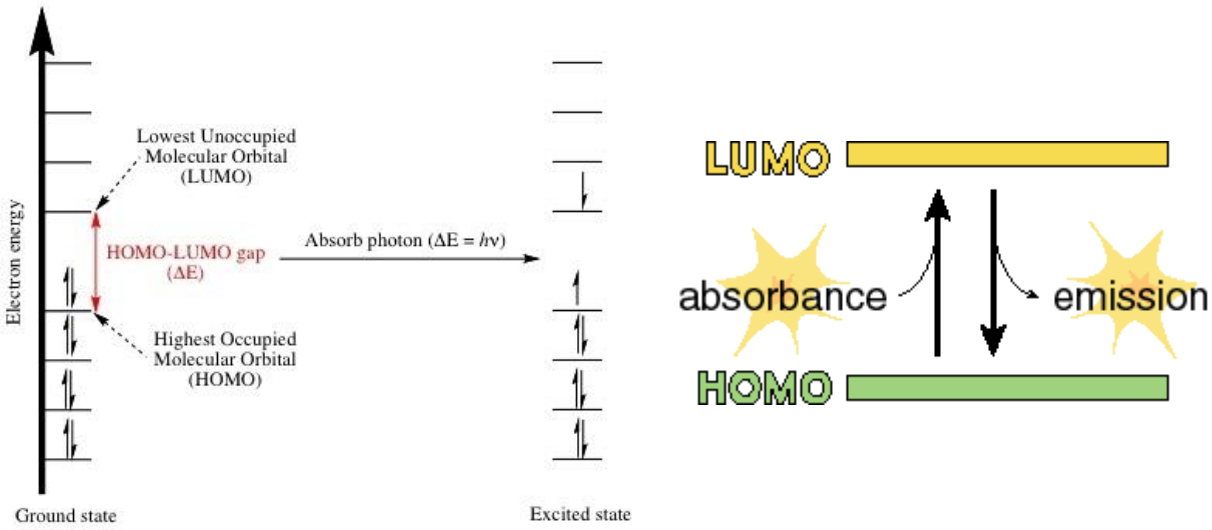


Figure1.1. Photoluminescence phenomena.

1.1.2. Electroluminescence:

Electroluminescence can be defined as the production of light from a material when an electric field is applied across it. It requires the excitation of the material into a higher energy state which can occur through various mechanisms and the subsequent relaxation of the material to a lower energy state resulting in the release of a photon. Long before organic materials were thought of as potential electroluminescent materials inorganic semiconductors were being used in light emitting diodes –LEDs The first example of electroluminescence was reported over 100 years ago[1] in a note to the editors of ***Electrical World.*** It was found that when a potential difference was applied across a crystal of carborundum (silicon carbide) a yellowish light was produced. Unfortunately, the discovery was not followed up and it was not until the mid-1920s that the LED was're-invented'[2].

1.1.2.1.Organic Electroluminescence:

Organic electroluminescence is the electronic excitation of organic compounds to emit light. To do this electrons are injected from the cathode into the LUMO. This forms radical anions with an electron (negatively charged) on the LUMO and radical cations with a hole (positively charged) on the HOMO (Figure 2).

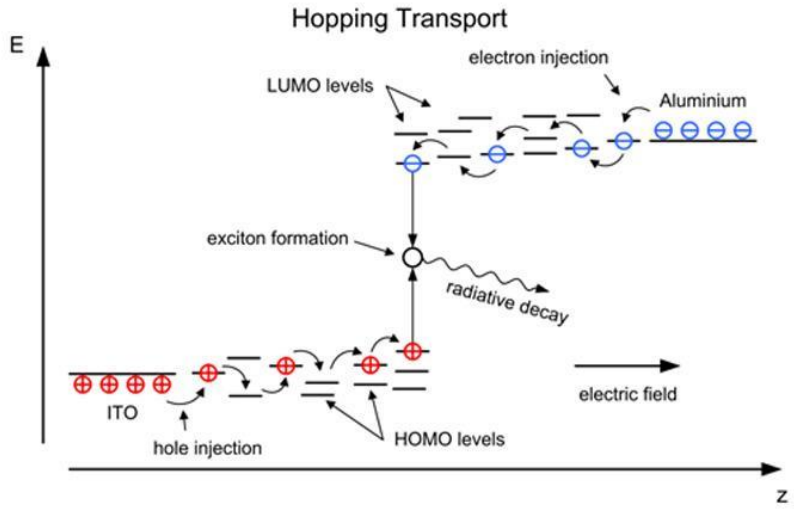


Figure 1.2. Electron and hole recombination.

These charges migrate within the organic material through a 'hopping' mechanism (vide infra)**.** If the charges combine within the emissive material they can form a molecular excited state. These excited states are called 'excitons' and are the emissive states that can release photons to decay to the ground state.

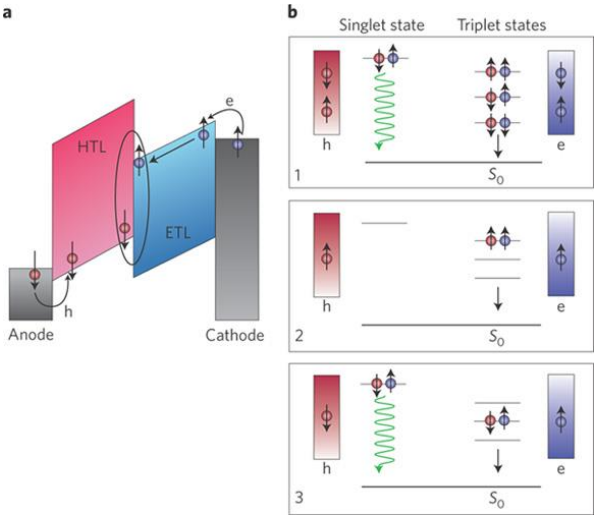


Figure 1.3. Exciton formation.

The total spin of the exciton can either be S=0 or S=l. The associated spin multiplicity (using 2S+1) of S=0 is 1 and of S=l is 3 hence these states are called singlets and triplets. With a total of 4 states and an equal chance of forming each state the probability of forming a singlet or triplet exciton is 25% and 75%, respectively. The singlet to triplet ratio has been measured experimentally [3,2c] and found to be within experimental limits of the expected 25:75, although more recent work suggests that in some polymeric materials a higher ratio of singlets can be generated [4,5b].

It is often found that there is an optimum amount of doping of the phosphorescent guest in the hostmaterial [5,6]. With too little phosphorescent dopant saturation ('concentration quenching') can occur due to the long lifetimes of phosphorescent excitons. If this occurs and the host is able to emit, emission will be observed from the host, which is likely to result in a hypsochromic (blue) shift in device emission as the host is likely to have higher energy emission. With an excess of phosphorescent dopant triplet-triplet annihilation can occur resulting in the reduction of triplet excitons. In triplet-triplet annihilation the total spin of the system is conserved when two triplet excitons combine and form a singlet exciton and singlet ground state (Figure 4).

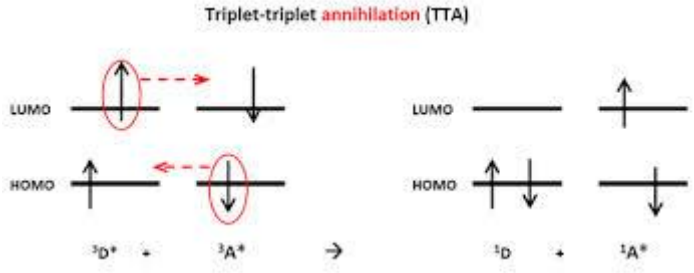


Figure 1.4. Triplet – triplet annulation

1.2. Organic Materials:

Organic Materials can either be small molecule or polymeric. Here the focus directed to small molecules. Fluorescent polymer light emitting devices, PLEDs, have had a huge impact in the field of OLEDs since the discovery of electroluminescence in a poly(phenylenevinylene) (PPV) derivative[7].

Small molecule organic materials for LEDs can be classified into two families - fluorescent and phosphorescent emitters.

1.2.1. Fluorescent Emitters:

Although singlet and triplet excitons were expected to be formed through charge recombination, only the singlet states were emitting, noting that the triplet states were expected to decay through a non-radiative pathway.

In 1987 Tang and VanSlyke published a revolutionary paper[9] describing a two layer device of a metal chelate complex (Alq_3) as the electron transporting and emitting layer and a diamine (TAPC) as the hole transporting layer. The inclusion of these transporting layers was found to greatly improve the efficiency of the device. The device structure is shown in the following figure 5.

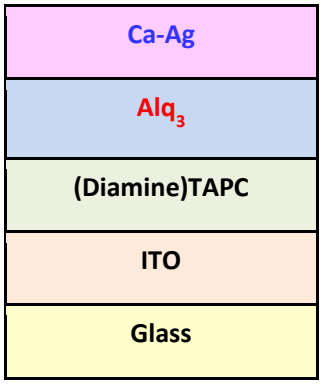
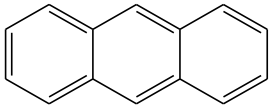


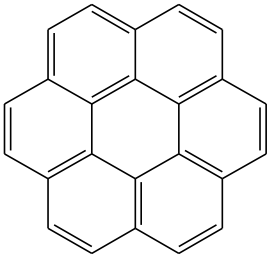
Figure 1.5. Device structure of two layer metal chelate complex

The advances in 1987 spurned on efforts to create new hole- and electron-transporting materials to improve device performance. Adachi and co-workers [10] developed a three layer device utilising an aromatic diamine (TPD) as the HTL and a perylene tetracarboxylic acid derivative (PV) as the ETL. Anthracene, coronene and perylene (depicted below) were chosen as the emissive materials as they fluoresce with different colours.

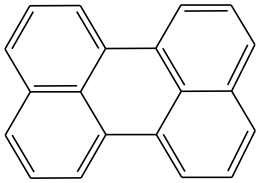
In 1989 Tang, VanSlyke and Chen [11] published a novel device structure based on their original two layer device. This new structure used a fluorescent dopant in the Alq_3 layer giving a device structure of ITO/diamine/Alq3 (3)/doped Alq3/Alq3 (3)/Mg:Ag.



Anthracene



Coronene



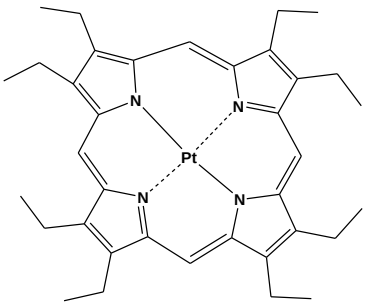
Perylene

1.2.2. Phosphorescent Emitters:

With fluorescent emitters' internal quantum efficiency effectively capped at 25% a new type of organic luminescent material was needed. The harvesting of both singlet and triplet states is necessary for increasing the efficiency of OLED devices. When a material exhibits this property under an induced electric field it is known as electrophosphorescence and leads to a theoretical 100% internal quantum efficiency.

The first example of electrophosphorescence was from benzophenone, reported in 1996 [18]. The device used consisted of three layers with the benzophenone guest dispersed in a poly(methylmethacrylate) host. It was found that the phosphorescence emission was very weak at room temperature (273 K) but was prevalent at 100 K at the turn on voltage of *ca.* 17 V. This is due to poor intersystem crossing in benzophenone and non-radiative processes being the primary method of exciton decay at room temperature. No transfer of triplet excitons was found between the host polymer and the benzophenone making it unsuitable for OLED applications as this will hamper the efficiency of the device.

Another material that exhibits electrophosphorescence is 2,3,7,8,12,13,17,18-octaethyl-21H-23H-porphine platinum (II) (PtOEP,).



PtOEP

The use of this material was investigated in 1998 by Baldo *et al*[19]. It was found that short range Marcus transfer dominates over longer range Forster transfer in the transfer of excitons. The inclusion of a metal centre into an organic ligand or chelate structure is a common method of increasing the efficiency of a material.

Chapter 2

Bipolar Hosts for Phosphorescent OLEDs

2.1. An overview of PhOLEDs

Since the invention of relatively efficient fluorescent organic light-emitting diodes (OLEDs) in 1987, [13] a new generation of flat-panel displays has emerged with a potential for capturing a substantial market share of consumable electronics, such as television sets and computer monitors. While full-color OLED displays require the emission of blue, green and red light, white OLEDs are potentially useful for efficient and inexpensive solid-state lighting and as backlights for liquid crystal displays. [14-16] Compared to molecular materials that can be vacuum-deposited into thin films, solution-processable materials, such as π-conjugated polymers and monodisperse oligomers, offer cost advantage and ease of scale-up to large-area thin films. Fluorescence or phosphorescence is responsible for light emission from organic luminophores. Electrophosphorescence is superior to electrofluorescence in terms of readily accessible internal quantum yield, 100 versus 25 %. Despite the intensive efforts worldwide over the past decade, device efficiency and lifetime have remained critical issues. For the fabrication of an efficient phosphorescent OLED, a triplet emitter is typically doped in a host material with sufficiently high triplet energy, E_T, to realize blue, green or red emission. [17-20] A higher E_T of the host than the guest ensures exciton transfer from the former to the latter where light emission occurs. In cases where the triplet emitters serve as charge traps, exciton formation is expected at the emitter without back-transfer to the host because of the higher E_T of the latter. Compared to exciton transfer from the host, charge trapping on the emitter as the source of phosphorescence is advantageous in terms of the higher internal quantum yield, [18, 21, 22] less concentration quenching because of the lower doping level, [21, 23] and the emission spectrum solely from the emitter, [23, 24] albeit at the higher driving voltage.[24]

Most of the existing triplet host materials are capable of preferentially transporting holes or electrons. [19, 25, 26] Charge injection and transport layers are added between electrodes and the emitting layer as needed to improve efficiency. [17-20, 25, 27] Nevertheless, charge recombination tends to occur close to the interface with the charge-transport layer for lack of bipolar transport capability in general of the emitting layer. [28, 29] Under a high current density pertaining to practical application, confinement of excitons to the interfacial region could expedite triplet-triplet annihilation, resulting in efficiency roll-off. [30-33] Furthermore, a narrow recombination zone is detrimental to operational stability because only a fraction of

molecules contribute to charge transport, exciton formation, and light emission. [34-36] to substantially improve device efficiency and lifetime, it is imperative that excitons be evenly distributed through the emitting layer and that the accumulation of charges and excitons at interfaces be prevented. To this effect, it has been demonstrated that mixed hosts can effectively decrease driving voltage while improving device efficiency sustainable at high current densities. [23, 24, 37-42] A typical phosphorescent layer is comprised of a host mixed with a charge-transport component at 25 to 50 wt%, to which 1 to 10 wt% of a triplet emitter is doped. The desired bipolar transport capability entails a high concentration of the charge-transport additive, at which doping level phase separation is destined to take place over time unless miscibility has been taken into account in the design of both components, thus adversely affecting long-term operational stability of OLEDs. Bipolar charge-transport host materials via chemical modification represent a viable approach to circumventing the potential phase-separation problem.

Generally, in these host/guest (dopant) systems, three roots can lead to dopant emission as shown in the following figure 6. [25-26]

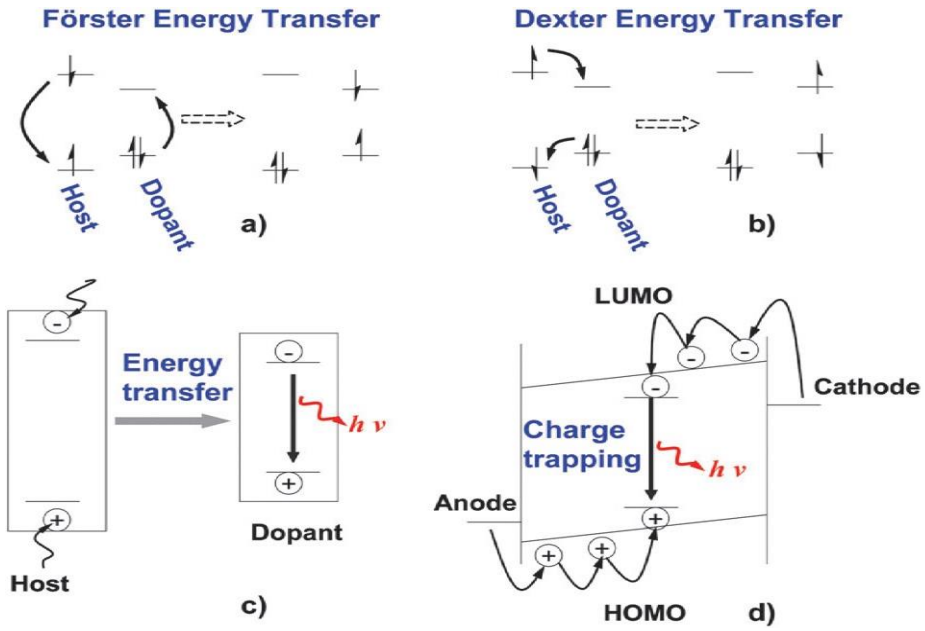


Figure 2.1.: Schematic representation of Forster energy transfer (a) and Dexter energy transfer (b); energy transfer (c) and charge trapping (d) alignment for dopant emission in host–dopant systems. *Chem. Soc. Rev.*, **2011**, 40, 2943–2970

i. The singlet excitons formed in the host under electrical excitation can be transferred to phosphor via Forster and Dexter energy transfer, and then singlet excitons in the phosphor are converted to triplet excitons by efficient intersystem crossing.

ii. The triplet excitons formed in the host can be transferred to phosphor to phosphor via Dexter energy transfer, and then radiative decay of triplet excitons (phosphorescence in the phosphors give light emission.

iii. The host and electrons injected from the anode and cathode can directly recombine on the phosphorescent guest molecule. The generated triplet excitons by charge trapping in phosphors relax to the ground state, which accompanies phosphorescent emission. [27]

Forster energy transfer is a Coulombic interaction between the host exciton and the dopant. This is a fast and long-range process (up to 10 nm) while Dexter energy transfer is an electron exchange interaction between the host exciton and the dopant, which is a short distance process (1.5–2.0 nm).

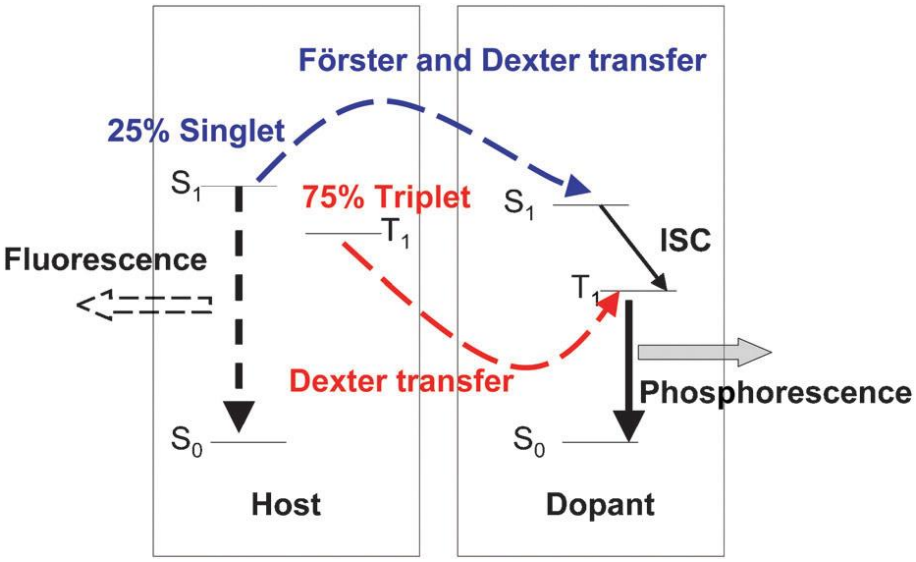


Figure 2.2.: Schematic energy-level alignment of the singlet-excited states (S_1), triplet-excited states (T_1) and ground states (S_0), as well as the energy transfer and light-emission processes in host–dopant systems. *Chem. Soc. Rev.*, **2011**, 40, 2943–2970

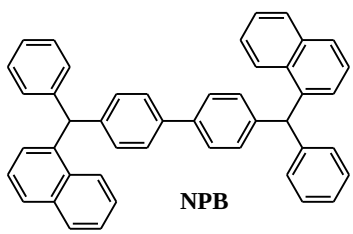
A bipolar compound can be constructed by chemically bonding an electron- and a hole-transport moiety with and without a finite extent of π-conjugation between the two moieties, resulting in conjugated and nonconjugated bipolar compounds, respectively. For all the conjugated bipolar host materials that have been developed for full-color emission, few non-conjugated bipolar compounds have been reported; of which none carry a flexible linkage consisting of σ-bonds between the two moieties. Conjugated and non-conjugated bipolar hybrid molecules without a flexible linkage tend to be rigid and bulky, thus limiting solubility and the ability to form morphologically stable glassy films. This study aims at a new class of non-conjugated bipolar hybrids comprising aliphatic linkages between the two charge-transport moieties.

To achieve efficient electro phosphorescence, the development of effective host materials is of importance. In the search for novel host materials for phosphorescent OLEDs, several requirements have to be considered. [29-32]

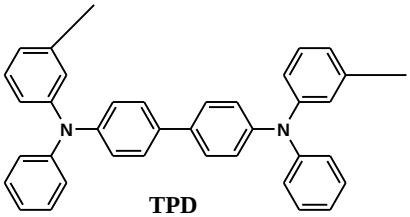
- The hosts should possess higher triplet energies than those of the dopant emitters to prevent reverse energy transfer from the guest back to the host, as well as confine triplet excitons in the emissive layer.
- The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of host materials should match with those of neighbouring active layers to reduce the hole and electron injection barrier, thus lowering the device driving voltages.
- The hosts are expected to have good and balanced charge carrier transport properties for the hole–electron recombination process and confinement of the exciton formation zone in the emissive layer.
- The host materials should have good thermal and morphological stability, which could reduce the possibility of phase separation upon heating, thus prolonging the device operational lifetime. Generally, a bulky and sterically hindered molecular configuration is preferable to enhance the glass transition temperature (Tg) and form morphologically stable and uniform amorphous films.

2.2. T**ypical hole transport materials**

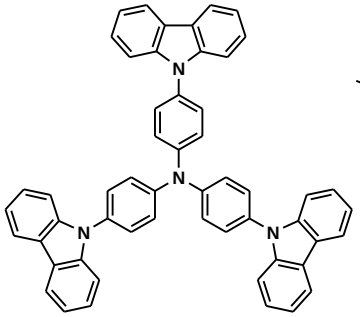
The molecular structure of hole transporting materials contain electron-donating moieties. Common examples are triphenylamine (TPA), diphenylamine, carbazole etc. a good hole transporting material should possess **i.** Good hole mobility, **ii.** A high glass transition temperature (Tg) to form morphologically and thermally stable thin film, **iii.** A proper HOMO level to confirm a low energy barrier for hole injection from anode and then to the emissive layer. **iv.** A suitable LUMO level to block electron injection from the emissive layer (EML) to the hole transporting layer (HTL), **v.** High triplet energy to confine triplet excitons in the EML.



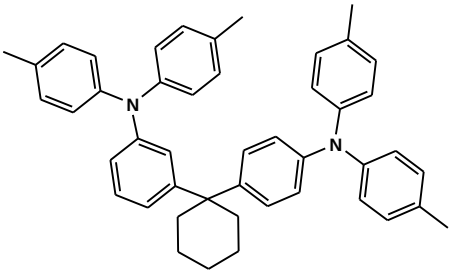
NPB



TPD



TCTA



TAPC

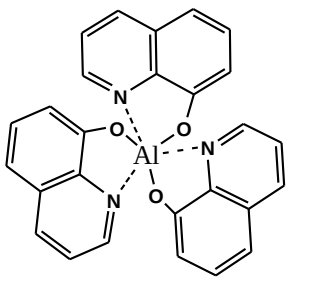
2.3. **Electron transport type host materials**

The electron transport type host materials basically contain electron withdrawing groups in their molecular structure and primarily transport electrons. In contrast to hole transporting host materials, electron transporting host materials are rare. Alq_3 was the first used electron transporting host material in the initial work of electrophosphorescence. however its low triplet energy of 2.0 eV hinders its application. It can only act as a host for deep red to near IR emitters. In order to broaden the recombination zone and balance the charge in EML,

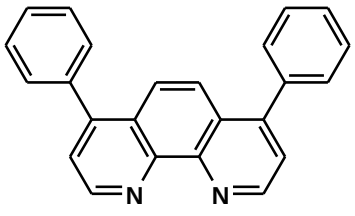
TPBI is generally used as electron transport type host in a mixed host system or double emissive layer. [26, 27, 28]

Electron transport type host materials are beneficial to achieve charge balance in electrophosphorescent devices. A desired electron transport type host material should have high triplet energy to prevent reverse energy transfer from the guest back to the host, normal thermal stability to form morphologically stable and uniform amorphous films, low electron injection barriers to reduce the driving voltage.

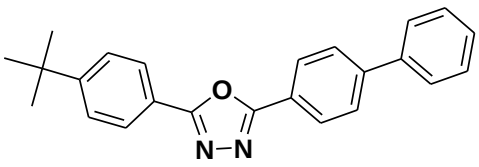
Various electron-transport type host materials are as follows:



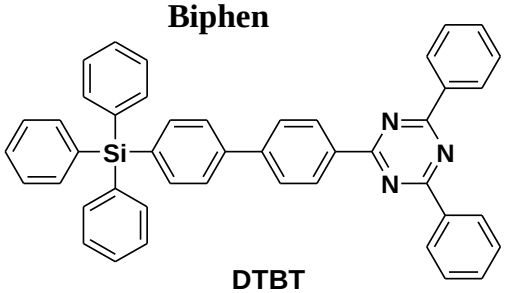
Aluminium tris(8-hydroxyquinoline)



Biphen



PBD



DTBT

2.4. Bipolar transport host materials

Most of the previously reported host materials are effectively capable of transporting holes and electrons. The recombination zone tends to occur close to the EML/ETL interface when using hole transport host. Similarly the recombination zone tend to occur at the EML/HTL interface when using an electron transport host.[30] the poor carrier mobility and unbalanced charges in the emitting layer have been proven to be due to the efficiency of OLEDs. PhOLEDs with narrow charge recombination zone could undergo triplet-triplet annihilation, which results in efficiency roll off due to a local accumulation of high density of triplet excitons, especially under high current densities.[25] hence the strategy of using double emissive layers with hole or electron transporting host in each emissive layer with both hole and electron transporting hosts have been presented to broaden the recombination zone and improve the device efficiency. [27, 28, 29] the two strategies make the fabrication of the device complicated. Also the mixed host may cause a potential phase separation problems. Hence to achieve highly efficient electrophosphorescence, host materials with balanced charge transport feature to generate broad charge recombination zones in the emissive layer are preferable.

Bipolar host materials have got great attention in the field of phosphorescent OLEDs because of their ability to provide more balance in electron and hole fluxes and simplify device structure. They have also extraordinarily high efficiency.

2.5. Molecular design of bipolar host materials

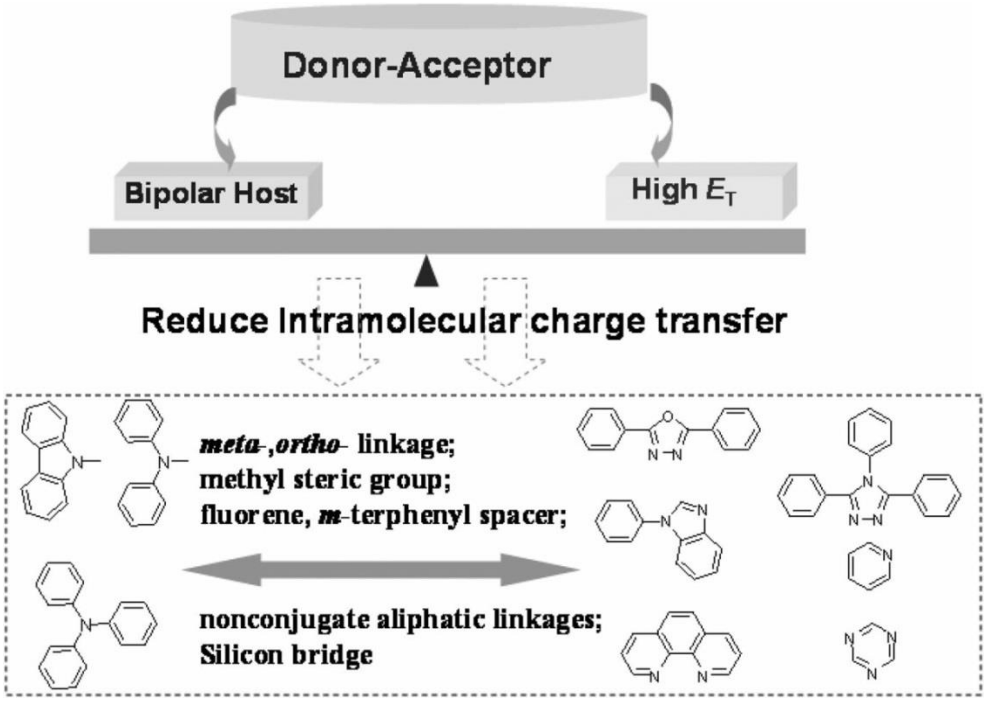
A suitable bipolar host in PhOLEDs must have some basic requirements.

i. Bipolarity to facilitate both hole and electron injection and transport. Bipolar compounds should have both electron-donating (comprised of arylamines such as carbazole, diphenylamine, triphenylamine etc.) and electron-withdrawing (consists of phenanthroline, oxadiazole, triazole, benzoimidazole, pyridine, phosphine oxide, triazine and so on) groups. ii. Good morphological and thermal stability to ensure device stability. iii. Matching HOMO and LUMO layers with those of the adjacent layers to reduce charge injection barriers and device driving voltage. iv. Higher triplet energy than the dopant to effectively prevent exothermic reverse energy transfer from the guest emitter to the host moiety.

However it is difficult for a bipolar host to achieve higher triplet energy because the electron withdrawing and hole transporting moieties in one molecule lowers the band gap of the material through intermolecular charge transfer, while the low triplet energy of the host can cause reverse energy transfer, which results in the decreased efficiency of PhOLEDs. To

overcome this problem molecular design of host materials focuses on introduction of π-conjugation layer between electron donating and electron withdrawing moieties. There are various methods available to reduce the intermolecular charge transfer (by incorporating p-type and n-type segment through the sp^3 hybridized atom. [32], by flexible non-conjugated sigma-bonded linkage between donor and acceptor moieties, connecting the two D-A through meta and/or ortho-linkage instead of para-position.

The triplet energy as well as electron mobility for various electron-withdrawing groups can vary. Hence except for the linkage mode, the selection of appropriate electron transporting groups is vital for bipolar transport hosts.



Scheme: Schematic description on molecular design of bipolar host materials through various linking spacers or linking topologies between electron-donating and electron-accepting moieties to reduce intramolecular charge transfer. *Chem. Soc. Rev.*, **2011**, 40, 2943–2970

2.6. Objective of the Proposed Work

In this work, bipolar host materials has been designed and synthesized, which can be used to control charge injection, transport and recombination in OLEDs. The molecular architecture, photophysical properties, thermal and morphological stabilities and OLED application of many organic bipolar host materials are summarized and discussed in relation of their effectiveness at enhancing optoelectronics applications. Efforts have been made to highlight the structure-property-performance relationship of various classes of bipolar host materials used to enhance the performance of OLEDs.

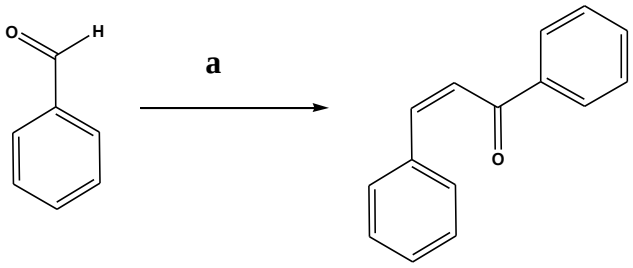
Chapter 3

EXPERIMENTAL SECTION

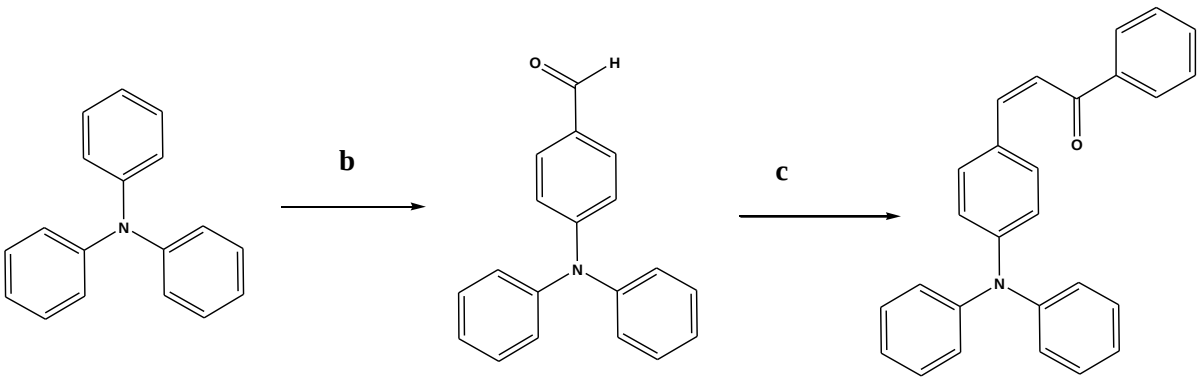
3.2 Experimental

Material Synthesis

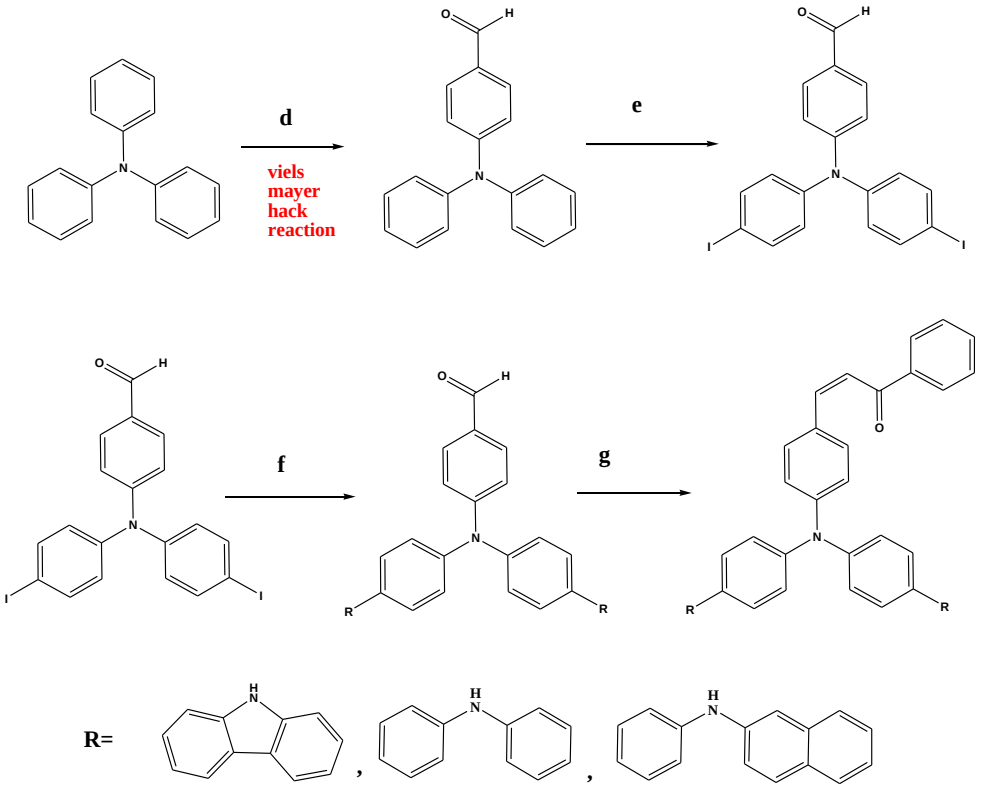
All chemicals, reagents, solvents were used as received from commercial sources without further purification except toluene, tetrahydrofuran (THF) and chloroform ($CHCl_3$) that had been distilled over sodium, benzophenone and P_2O_5 respectively. Those reactions which are moisture sensitive were carried out under nitrogen and anhydrous conditions unless noted otherwise. 1H NMR spectra were acquired in $CDCl_3$ with an Advance-400 spectrometer (400 MHz) at 298 K using trimethylsilane (TMS) as an internal standard. Elemental analysis was carried out by Quantitative Technologies, Inc. Molecular weights were measured with an ESI Mass spectrometer (Perkin Elmer, USA). The target compounds were synthesized and purified according to reaction Scheme 1-3 following the procedures described below.



Scheme 1: Reagents and Conditions: a= C_6H_5OH, NaOH, C_2H_5OH, H_2O;

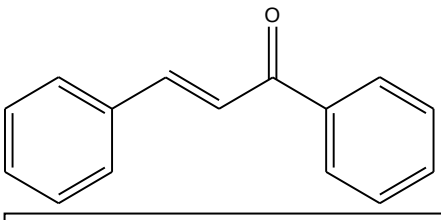


Scheme 2: Reagents and Conditions: b=$POCl_3$, DMF, 0^0C, $CHCl_3$, 100^0C; c= C_6H_5OH, NaOH, C_2H_5OH, H_2O;



Scheme 3: Reagents and Conditions: d=$POCl_3$, DMF, 0^0C, $CHCl_3$, 100^0C; e= KI, KIO_3, CH_3COOH, 80^0C, 4 hr.; f= diphenylamine or carbazole, 1,2-dichlorobenzene, CU, K_2CO_3, 18-crown-6, reflux, 24 hr.; g= C_6H_5OH, NaOH, C_2H_5OH, H_2O;

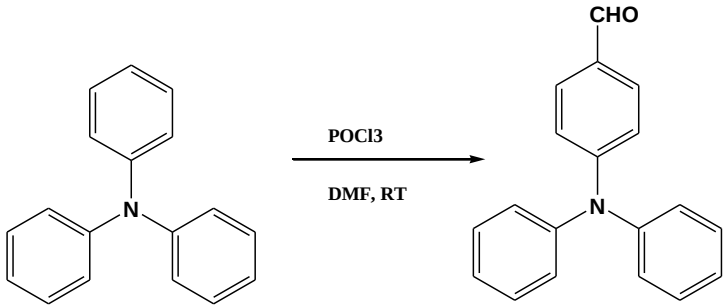
Synthesis of chalcone **(Benzaldehyde – Acetophenone):** Benzaldehyde [1 g (9.423 mmol)] and NaOH [0.376 g (0.9.423 mmol)] were added into the mixture of 12mL of water and 15mL of ethanol, and then 2.26 g (18.843 mmol) of 1-phenylethanone was added. The mixture was heated and stirred at 90 ^{0}C for 4 hr. After cooling, the mixture was filtered and washed with plenty of water and then dried up at room temperature to produce 2.2 g of white yellow powder, yield of 85%. 1H NMR (CDCl3, 400 MHz): 7.90 (d, J = 7.2 Hz, 3H), 7.64 (t, J = 7.2 Hz, 2H), 7.48–7.52 (t, J= 8, 3H), 7.31–7.33 (d, J= 10.08, 2H), 7.22 (t, J = 15.2 Hz, 1H), 7.13 (d, 1H),



Benzaldehyde – Acetophenone

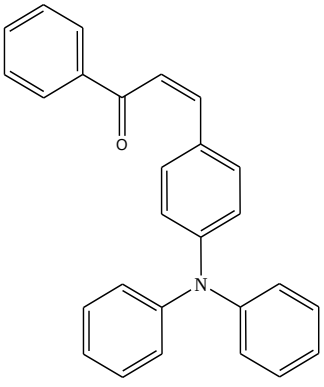
Synthesis of 4-(diphenylamino)benzaldehyde **(TPA – CHO):** Dimethylformamide (DMF) (1.71mL, 22.04mmol) was taken in a clean-dried two neck round bottom flask and added drop wise phosphorous oxy chloride (2.05ml, 22.04mmol) at 5^{o}C. After 30min,

triphenylamine (TPA) (2g, 8.163mmol) in DMF (15mL) was added drop wise to reaction mixture at same temperature. The resulting mixture was stirred for overnight at RT, then poured into water and neutralized with diluted sodium hydroxide solution (up to pH 6). Then extracted with chloroform and washed with brine solution followed by dried with sodium sulphate. The crude product was washed with diethyl ether: hexane (3:7) mixture solvent and recrystallization in ethanol to get 2g pure 4-1 (90%) with pale yellow colored fine solid.**^{1}H-NMR Data** ($CdCl_3$, 400MHz): δ 9.82 (s, 1H), 7.70 (d, 2H), 7.38-7.34 (m, 2H), 7.25-7.24 (m, 2H), 7.20-7.15 (m, 6H), 7.03 (d, 2H). **^{13}C-NMR Data** ($CdCl_3$, 100MHz): δ 153.3, 146.1, 131.3, 129.7, 129.0, 126.3, 125.1, 119.3.



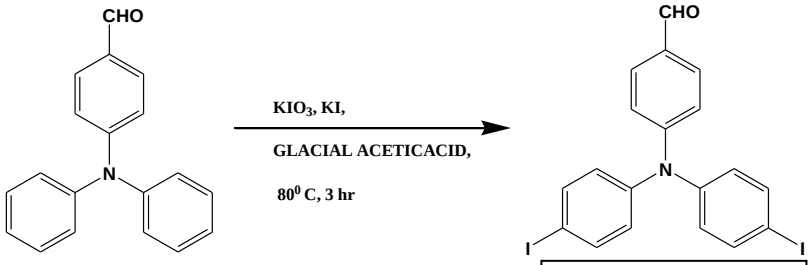
TPA – CHO

Synthesis of (*Z*)-3-(4-(diphenylamino)phenyl)-1-phenylprop-2-en-1-one **(TPA-Acetophenone)**: TPA-CHO [0.5 g (1.831 mmol)] and NaOH [0.08 g (1.831 mmol)] were added into the mixture of 30mL of water and 25mL of ethanol, then 0.24 g (3.663 mmol) of 1-phenylethanone was added. The mixture was heated and stirred at 90 ^{0}C for 4 hr. After cooling, the mixture was filtered and washed with plenty of water and then dried up at room temperature to produce 0.3 g of yellow powder, yield of 80%. 1H NMR (CDCl3, 400 MHz): 8.01 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 16.0 Hz, 1H), 7.58–7.54 (t, 1H), 7.51–7.48 (m, 4H), 7.39 (d, J = 16.0 Hz, 1H), 7.34–7.29 (m, 4H), 7.18–7.09 (m, 6H), 7.03 (d, J = 8.0 Hz, 2H).



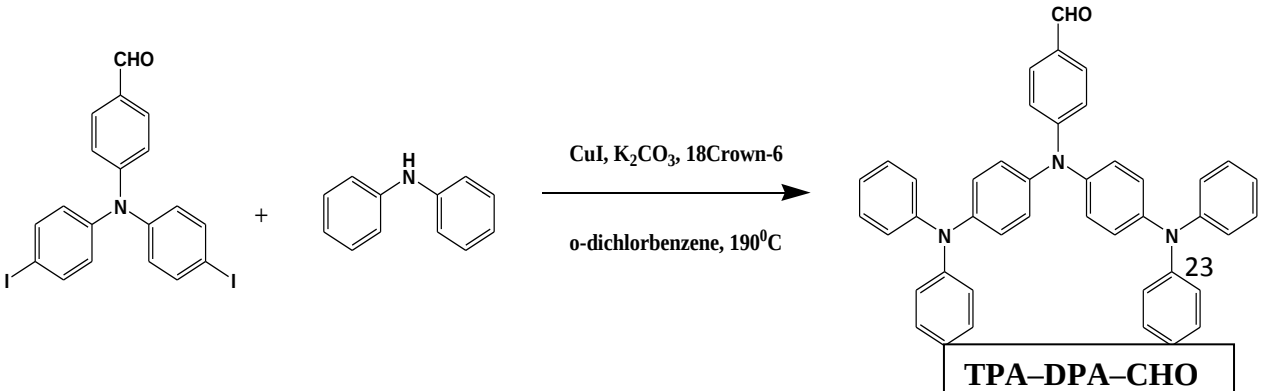
TPA-Acetophenone

Synthesis of 4-(bis(4-iodophenyl)amino)benzaldehyde **(TPA – CHO –I_2):** Under rapid stirring, 4 (2.73 g, 10 mmol) was dissolved in glacial acetic acid (10 mL) and KI (3.32 g, 20 mmol) and KIO_3 (6.42 g, 30 mmol) were added; the reaction mixture was stirred for 3 h at 70 ^{0}C. After cooling, the solid was filtered off and washed thoroughly with water (50 mL) and dichloromethane (100 mL). The aqueous phase was extracted several times with dichloromethane. The combined organic phases were washed with a diluted ammonia solution (10%) until pH becomes nearly 8, with a saturated $NaHCO_3$ solution, and with saturated brine and dried over $MgSO_4$. After removal of the solvents, the crude compound was stirred for 15 min in boiling ethanol (50 mL); the solution was cooled, and the pure product was isolated by filtration (4.2 g, 80%). Yellow solid, **^{1}H-NMR Data** (DMSO, 400MHz): δ = 9.859 (s, 1H), 7.72 (d, 2 H, 7.64 (d, 4H), 7.07 (d, 2H), 6.91 (d, 4H).



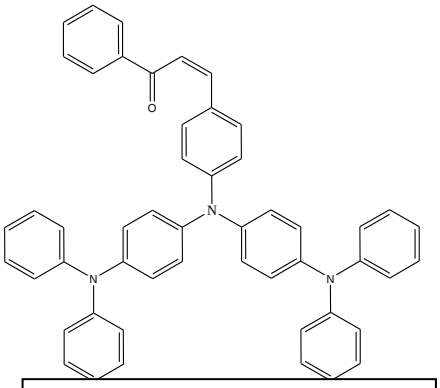
TPA – CHO –I_2

Synthesis of 4-(bis(4-(diphenylamino)phenyl)amino)benzaldehyde **(TPA–DPA–CHO):** In a 250mL round bottom flask, 4-[N,N-di(4-iodophenyl)amino]- benzaldehyde (1 gm, 1.9 mmol), diphenylamine (0.98 gm, 5.7mmol), potassium carbonate (2.09 gm, 15.2 mmol) copper iodide (0.28 gm, 1.52 mmol) and 18 – crown – 6 (0.01 gm, 0.38 mmol) were reflexed in 1,2 – dichlorobenzene (15 mL) for 48 hrs, under nitrogen atmosphere. The inorganic components are filtered while hot and then the product was precipitated in methanol. The crude product was purified by column chromatography on silica (petroleum ether : dichloromethane = 1:1, v/v) to afford the product as yellow powder (yield: 59 %). **^{1}H-NMR Data** (DMSO, 400MHz): δ = 9.81 (s, 1H), 8.156 (s, 1H), 7.953 (s, 1H), 7.752 (m, 5H), 7.55 (d, 2H), 7.223(t, 5H), 7.012 (m, 11H), 6.793(t,4H). **^{13}C NMR data** (400MHz, DMSO-d6): δ= 190.97, 141.45, 140.82, 140.56, 140.15, 132.10, 130.02, 129.80, 127.91, 125.16, 125.11, 123.75, 115.40.



TPA–DPA–CHO

Synthesis of TPA–DPA–Acetophenone: TPA-DPA-CHO [0.2 g (0.33 mmol)] and NaOH [0.013 g (0.330 mmol)] were added into the mixture of 12mL of water and 10mL of ethanol, then 0.079 g (0.66 mmol) of 1-phenylethanone was added. The mixture was heated and stirred at 90 ^{0}C for 4 hr. After cooling, the mixture was filtered and washed with plenty of water and then dried up at room temperature to produce 0.3 g of yellow powder, yield of 80%. 1H NMR (CDCl3, 400 MHz): 9.814 (d, 1H), 8.156 (d, 1H), 7.953 (t, 1H), 7.752 (m, 5H), 7.555 (d, 2H), 7.204 (m, 5H), 7.027 (d, 11H), 6.829 (m, 4H),



TPA–DPA–Acetophenone

2.4. **Instruments and photo-physical characterization:**

1H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane. All photoluminescence (PL) spectra were measured with a Fluorescence spectrometer (Horiba Jobin, USA). Absorption spectra of the compounds were measured with Shimadzu Spectrophotometer (UV-2250) in the range of 200-800 nm. Thermal properties were measured with Perkin-Elmer-TGA 7 under N2 atmosphere. All measurements were carried out in air at room temperature.

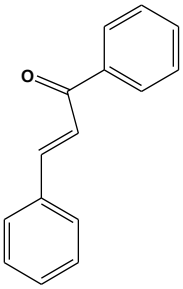
Chapter 4

Results and Discussions

4.1. **Photo-physical properties:**

From the UV-Visible spectral data it is clear that Benzaldehyde-Acetophenone (Fig. 4.1.) molecule absorbs at 252, 280, 314 nm out of which the absorption at 252 nm is the short absorption peak and the absorption at 314 is the broad absorption peak. As this molecule is less conjugated hence it shows absorption near green region. The absorption spectra of TPA-Acetophenone in CH_2Cl_2 (10^{-4} mol/L) shown in (Fig. 4.2) have two strong broad absorption bands at 290 and 420nm, respectively, which are ascribed to the π to π* transitions of conjugated chain, Compared with the absorption spectrum of N,Ndiphenyl- 4-styrylaniline[38, 39], which possesses a molecular structure similar to that of TPA-Acetophenone. The π to π* transitions of TPA-Acetophenone shift to visible region owing to enlargement of π-conjugated chain and introduction of strong electron donor, the triphenylamine group. The TPA-Carbazoleacetophenone (Fig 4.4.) accepts shows maxima peak at 247, 292, 317, 413 nm. But the peak at 292 nm shows sharp absorption and at 413 nm shows broad absorption peak. Hence the corresponding colour to this absorption is being seen. The absorption peak corresponds to HOMO to LUMO transition which again refers to n to π* and π to π* transition. The TPA-DPA-Acetophenone (Fig 4.3.) shows absorption near 291 and 362 nm. Among which the absorption peak at 362 nm is the maximum absorption peak and corresponds to the HOMO to LUMO transition. DFT calculations can precisely predict the nature of transition.

From the UV-Vis absorption spectroscopy it is clearly understood that with increase in conjugation we are getting redshift which indicates that with increase in conjugation of the donor molecule the HOMO-LUMO energy gap must be decreasing and by virtue of which we are getting a redshift in the absorption pattern and the corresponding colour is being observed.



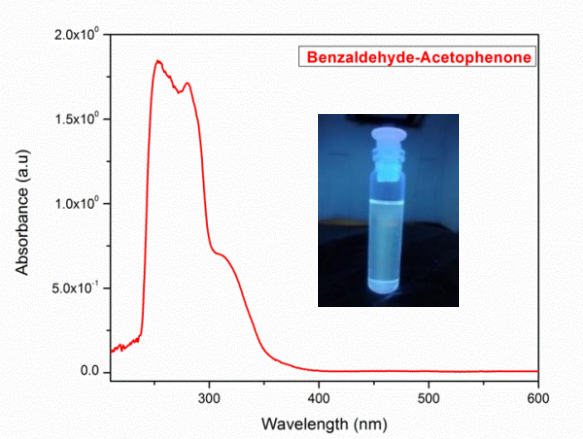
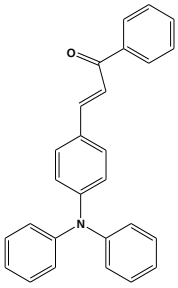


Fig. 4.1-UV-Vis spectroscopy of Benzaldehyde-Acetophenone



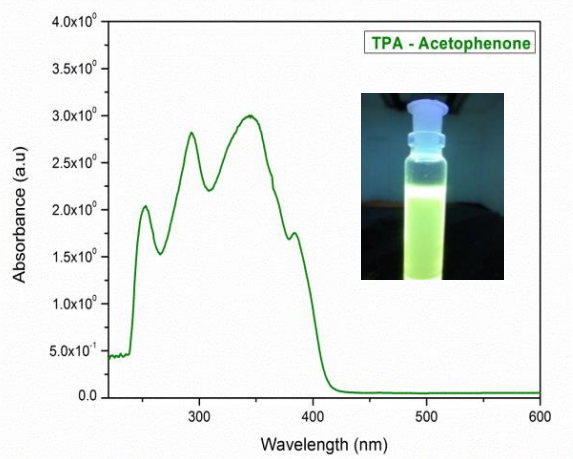
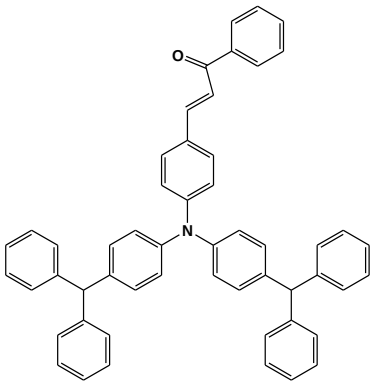


Fig. 4.2-UV-Vis spectroscopy of TPA-Acetophenone



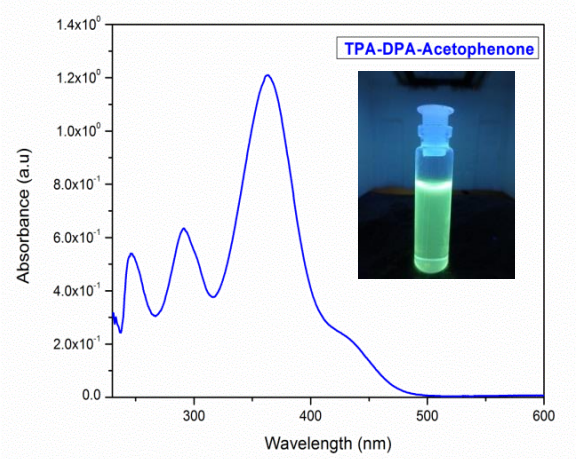
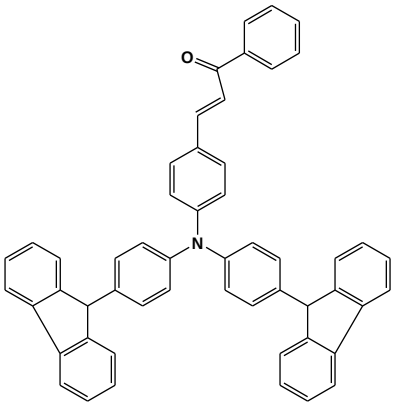


Fig. 4.3-UV-Vis spectroscopy of TPA-DPA-Acetophenone



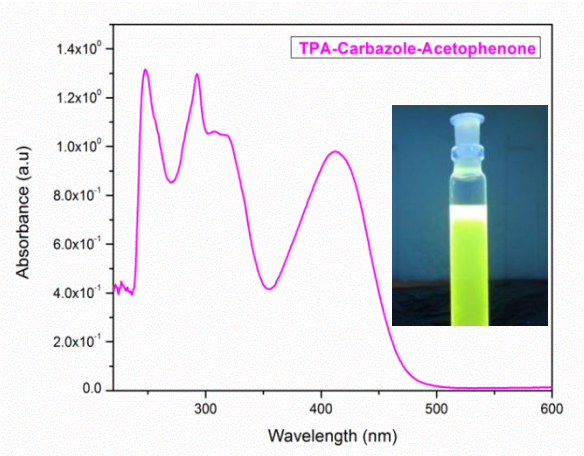


Fig. 4.4-UV-Vis spectroscopy of TPA-CARBAZOLE-Acetophenone

Mass spectra:

The mass spectra of TPA-Acetophenone molecule (Fig 4.5) shows the mass of the molecule is 376 this matches with the mass of the compound. This indicates that our molecule doesn't undergo any sort of further breakdown or splitting to small molecules during the analysis.

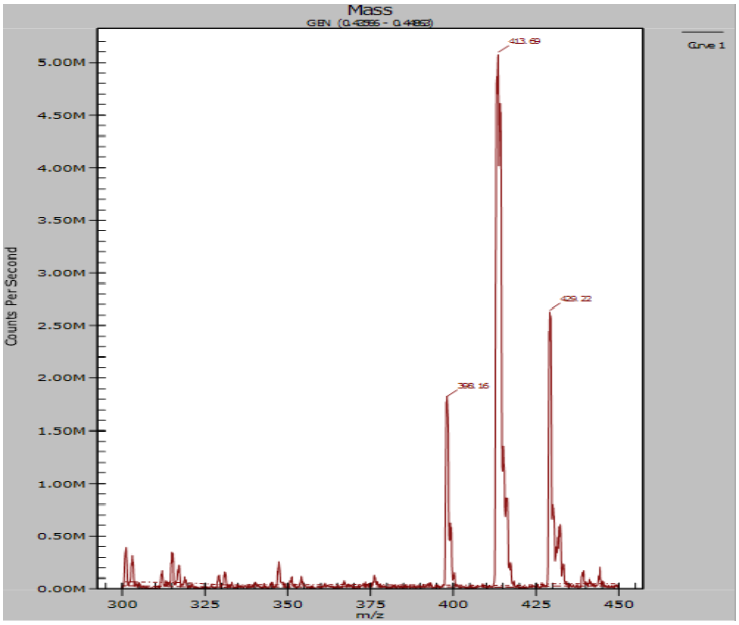


Fig 4.5- mass spectra of TPA-Acetophenone

4.2. TGA-DTA analysis:

Thermal properties of TPA-Acetophenone (Fig 4.6) and other compounds were studied by differential scanning calorimetry (DSC). Temperature increased from 20 ^{0}C with a rate of 10 ^{0}C/min. As shown in Fig. 4.6-4.9, there exist two weak absorption of heat at 34 and 100 ^{0}C, respectively. The first one is ascribed to the verification absorption of TPA-Acetophenone, and the latter one corresponds to the vaporization heat absorption of water. A sharp absorption of heat peaks at 130 1C, indicating that the melting process of TPA-Acetophenone occurs. Since normal working temperature of white LEDs is below 100 ^{0}C [41], it is clear that TPA-Acetophenone is thermal stable enough for practical applications.

The TPA-DPA-Acetophenone (Fig. 4.7) molecule shows absorption of heat at 58.9 and 186.8 ^{0} C, which indicates the melting point of the sample, is around 194 ^{0}C. TPA-Carbazole (Fig. 4.8) molecule shows absorption peak of heat at around 269^0 C and melting point of the sample being around 319 ^{0}C. Benzaldehyde-Acetophenone (Fig.4.9) molecule shows absorption around 72 and 305 ^{0}C and melting point of the sample being 317 ^{0}C.

Henceforth from the above calibration of data it is quite clear that all of our samples are the potent candidates for PhOLED devices and can be used as bipolar host materials. But however among the four synthesized compounds the TPA-Carbazole molecule is the best to be used as a bipolar host material as this compound has highest melting point and it doesn't absorb any hear in the device operational temperature range of 100 ^{0}C.

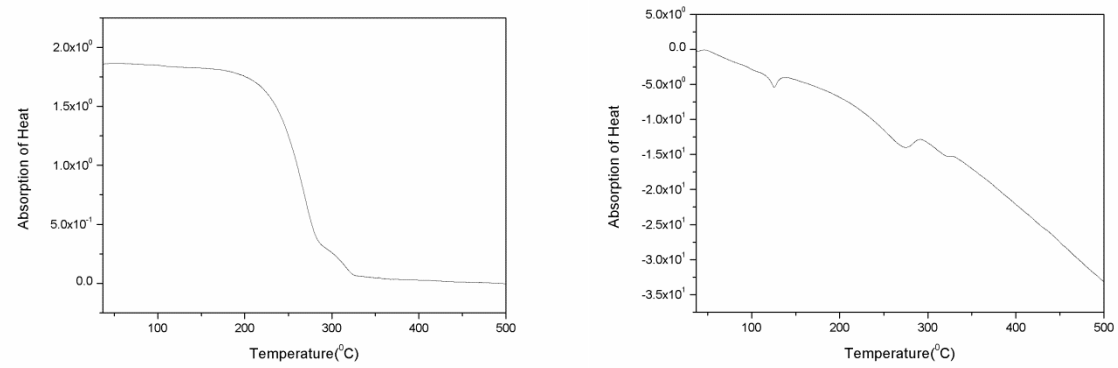


Fig 4.6: TGA-DTA of TPA-Acetophenone

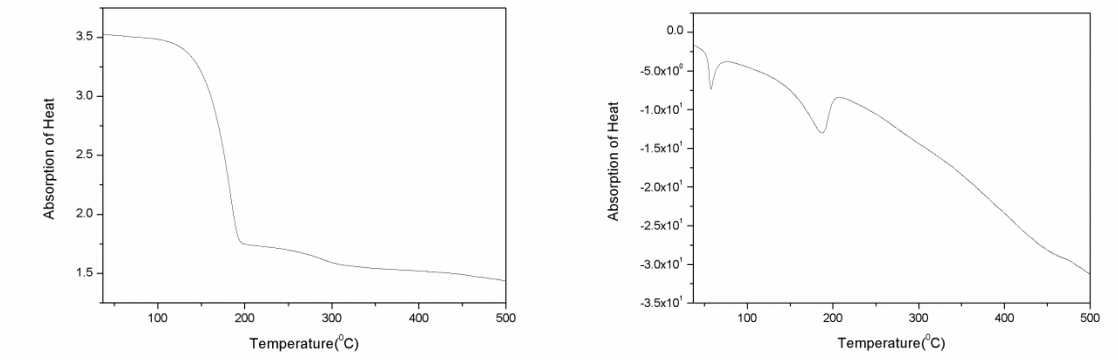


Fig 4.7: TGA-DTA of TPA-DPA-Acetophenone

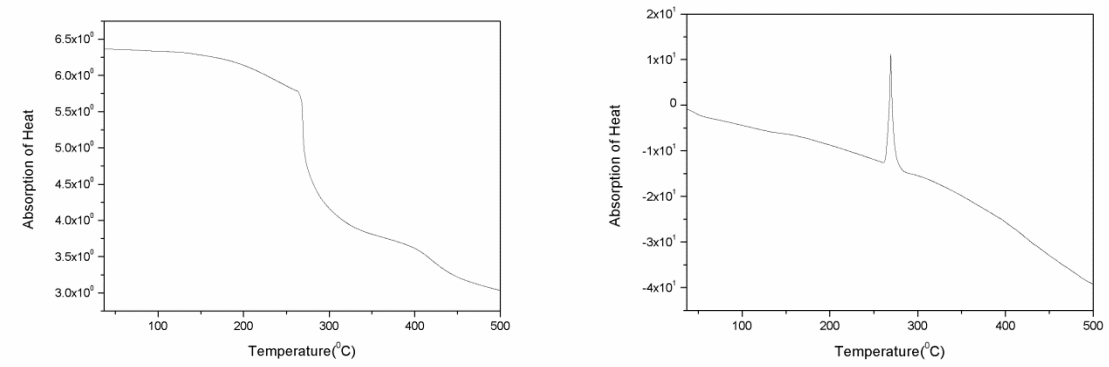


Fig 4.8: TGA-DTA of TPA-Carbazole-Acetophenone

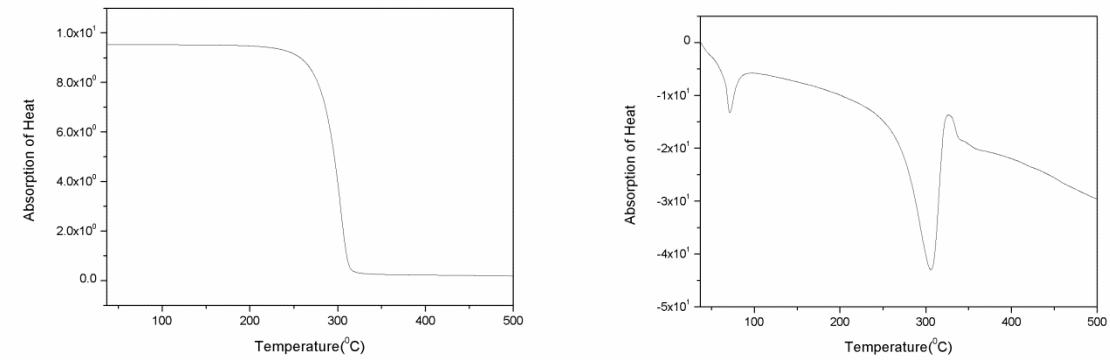


Fig 4.9: TGA-DTA of Benzaldehyde-Acetophenone

4.3.Fluorescence studies:

The Photo Luminescence Spectroscopy of the TPA-Acetophenone and TPA-Carbazole-Acetophenone compounds were measured at 344 and 413 nm emission range respectively. The emission patterns are obtained as shown in the Fig.4.10 which indicates that TPA-Acetophenone emits at 507 nm and TPA-Carbazole-Acetophenone emits at 544 nm respectively. Also with increase in the conjugation at the hole transporting moiety side the emission wavelength approach toward red shift due to probable decrease in HOMO-LUMO energy gap. The intensity of emission of TPA-Carbazole-Acetophenone is also more than that of TPA-Acetophenone. Therefore the latter one is a potent candidate for bipolar host material.

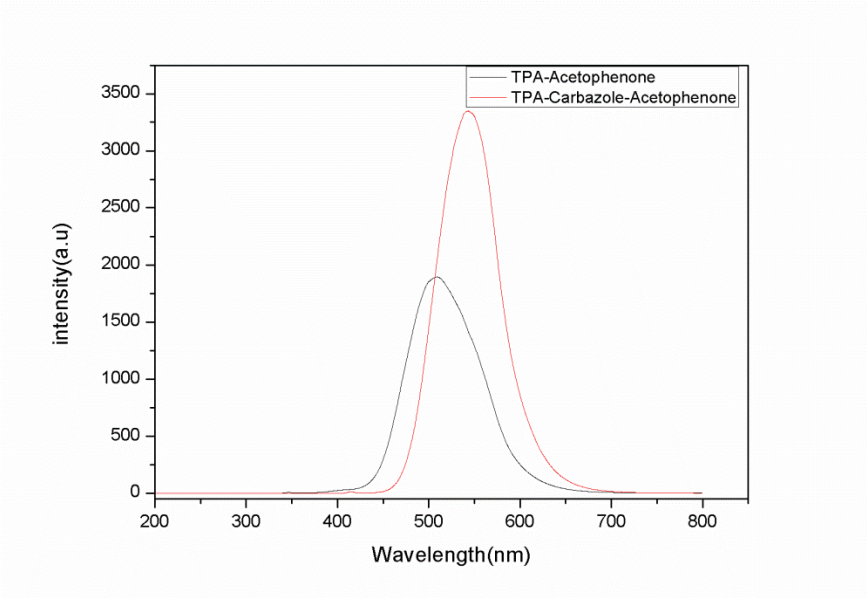


Fig 4.10: PL spectra of TPA-Acetophenone and TPA-Carbazole-Acetophenone

Chapter 5

Conclusion and Outlook

5.1. **Summary:** In our synthesized compounds when the conjugation of electron transporting group is increasing we are obtaining a emission colour which tends towards Red shift. The basic reason is that as we go on increasing the conjugation the HOMO and LUMO energy gap decreases and consequently a Red shift is obtained. We can play with bipolar host structure and tune the structure to get an appropriate structure of our desire, which yields a large variety of substrate scope which can be implemented as bipolar host materials in PhOLEDs.

To achieve high efficiency PhOLEDs, the appropriate host materials are of equal importance to the phosphorescent emitters. In this work we have synthesized novel bipolar host materials that can have a potent application in PhOLEDs. The key qualities of the host materials like relationship between the molecular structure of hosts and their thermal, electrochemical and photophysical properties have been addressed. In general, to design a host for a blue phosphor, a high enough triplet energy is main concern; to design a host for green or red phosphor, relatively narrow energy gap and matched HOMO and LUMO levels with adjacent layers are desirable. The good charge transporting ability and high glass transition temperatures of host materials benefit the device performance.

5.2. **Future work**: Typical properties of host materials like triplet energy gap, charge transporting ability, HOMO/LUMO level, and glass transition temperature should be addressed. Up to date, green and red PhOLEDs with 100% internal quantum efficiency have been achieved, but highly efficient and stable blue PhOLEDs remain to be further developed. Moreover, the low efficiency and instability of blue PhOLEDs become a bottleneck to the development of efficient and stable white PhOLEDs. In this regard, a bipolar host capable of hosting a blue phosphor can play a vital role because a bipolar host could not only broaden the exciton-formation zone, consequently reduce efficiency roll-off, but also simplify the device structures by the employment of a single emitting layer comprising of a bipolar host and two or more phosphors. Systematic engineering is required to achieve highly efficient and stable PhOLEDs. It is only through the close collaboration between both chemists and physicists that continuous promising advances in this area can be attained. We hope the host materials will render highly efficient, stable, and solution-processable phosphorescent OLEDs for commercial application.

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